

AD-A137 203

THEORETICAL CHEMICAL CALCULATIONS ON MOLECULES OF AIR  
FORCE INTEREST(U) FRANK J SEILER RESEARCH LAB UNITED  
STATES AIR FORCE ACADEMY CD L DAVIS ET AL. NOV 83

1/1

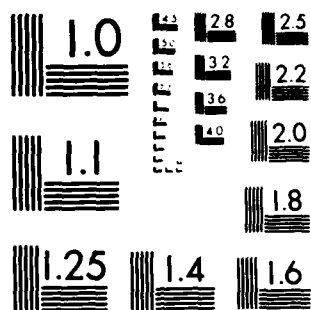
UNCLASSIFIED

FJSRL-TR-83-0014

F/G 7/4

NL


END  
DATE  
FILMED  
2-84  
DTIC



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A



AD A 137203



2

FRANK J. SEILER RESEARCH LABORATORY

FJSRL-TR-83-0014

November 1983

Theoretical Chemical Calculations  
on Molecules of Air Force Interest

Larry P. Davis  
Almon G. Turner  
R. Martin Guidry  
Thomas B. Menard

DTIC  
ELECTE  
S JAN 25 1984 D  
D

APPROVED FOR PUBLIC RELEASE;  
DISTRIBUTION UNLIMITED.

AIR FORCE SYSTEMS COMMAND  
UNITED STATES AIR FORCE

84 01 24 100

This document was prepared by the Molecular Dynamics Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, CO. The research was conducted under Project Work Unit number 2303-F4-03. Larry P. Davis was the project scientist.

When U.S. Government drawings, specifications or other data are used for any purpose other than a definitely related government procurement operation, the government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the government may have formulated, furnished or in any way supplied the said drawings, specifications or other data is not to be regarded by implication or otherwise, as in any manner licensing the holder or any other person or corporation or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

Inquiries concerning the technical content of this document should be addressed to the Frank J. Seiler Research Laboratory (AFSC), FJSRL/NC, USAF Academy, CO 80840. Phone AC 303 472-2655.

This report has been reviewed by the Commander and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

*Larry P. Davis*

Larry P. Davis  
Director of Research

*Armand A. Fannin, Jr.*

Armand A. Fannin, Jr, Lt Colonel  
Director, Chemical Sciences

Kenneth E. Siegenthaler, Lt Colonel  
Chief Scientist

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

Printed in the United States of America. Qualified requestors may obtain additional copies from the Defense Documentation Center. All others should apply to:

National Technical Information Service  
6285 Port Royal Road  
Springfield, Virginia 22161

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

## REPORT DOCUMENTATION PAGE

ADA

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS None	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Distribution Unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) FJSRL-TR-83-0014		5. MONITORING ORGANIZATION REPORT NUMBER(S) N/A	
6a. NAME OF PERFORMING ORGANIZATION Frank J. Seiler Research Lab	6b. OFFICE SYMBOL (If applicable) FJSRL/NC	7a. NAME OF MONITORING ORGANIZATION N/A	
6c. ADDRESS (City, State and ZIP Code) The Frank J. Seiler Research Laboratory (AFSC) USAF Academy, Colorado Springs, CO 80918		7b. ADDRESS (City, State and ZIP Code) N/A	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Frank J. Seiler Research Lab	8b. OFFICE SYMBOL (If applicable) FJSRL/NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N/A	
8c. ADDRESS (City, State and ZIP Code) The Frank J. Seiler Research Laboratory (AFSC) USAF Academy, Colorado Springs, CO 80918		10. SOURCE OF FUNDING NOS.	
		PROGRAM ELEMENT NO.	PROJECT NO. 2303
		TASK NO. F4	WORK UNIT NO. 03
11. TITLE (Include Security Classification) Theoretical Chemical Calculations on Molecules of Air Force Interest			
12. PERSONAL AUTHOR(S) Larry Davis, Almon Turner, R. Martin Guidry, and Thomas Menard			
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Yr., Mo., Day) November 1983	15. PAGE COUNT
16. SUPPLEMENTARY NOTATION N/A			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB. GR.	
0704		Energetic Materials	
2005		Theoretical Chemistry	
		Electrochemistry	
		Molecular Orbital Calculations	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>Semiempirical molecular orbital calculations are reported in areas of basic chemical Air Force research: explosives, propellants, electrochemistry, and the oxygen-iodine laser system. This report is a final report on Work Unit 2303-F4-03, "Molecular Orbital Calculations of Energetic Materials".</p> <p>These molecular orbital calculations have given useful insights in each of these areas. In particular, <del>we have</del> made substantial progress on understanding TNT thermochemical decomposition. <i>has been made.</i></p>			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS <input type="checkbox"/>		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Captain Larry Davis	22b. TELEPHONE NUMBER (Include Area Code) 472-2681	22c. OFFICE SYMBOL DF SQ/DFC	

DD FORM 1473, 83 APR

EDITION OF 1 JAN 73 IS OBSOLETE.

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

**BLANK PAGE**

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

THEORETICAL CHEMICAL CALCULATIONS  
ON MOLECULES OF AIR FORCE INTEREST

Larry P. Davis  
Almon G. Turner  
R. Martin Guidry  
and  
Thomas B. Menard

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A/1	

November 1983



Approved for public release; distribution unlimited

Directorate of Chemical Sciences  
The Frank J. Seiler Research Laboratory  
United States Air Force Academy  
Colorado Springs, Colorado 80840

### Abstract

Semiempirical molecular orbital calculations are reported in areas of basic chemical Air Force research: explosives, propellants, electrochemistry, and the oxygen-iodine laser system. This report is a final report on Work Unit 2303-F4-03, "Molecular Orbital Calculations of Excited Species". Work will be continued under a new work unit, 2303-F3-07, "Theoretical Chemical Calculations of Energetic Materials".

These molecular orbital calculations have given useful insights in each of these areas. In particular, we have made substantial progress on understanding TNT thermochemical decomposition.



## Table of Contents

Abstract . . . . .	i
List of Tables . . . . .	iii
1. Introduction . . . . .	1
2. Theoretical Methods. . . . .	2
3. Electrochemical Calculations . . . . .	4
4. Aluminum Calculations. . . . .	6
5. Oxygen Singlet-Delta Calculations. . . . .	7
6. Decomposition of Explosives and Propellants. . . . .	9
7. Sulfur Nitrogen Calculations . . . . .	26

### List of Tables

I. Standard Enthalpies of Reaction. . . . .	.13
II. Activation Enthalpies for 1-Nitropropene System . . . . .	.15
III. Results of DMNA Calculations . . . . .	.25

## Chapter 1

### INTRODUCTION

Since its inception in December 1976, Work Unit 2303-F4-03, entitled "Molecular Orbital Calculations of Excited Species", has sought to perform theoretical chemical calculations on molecules of Air Force interest. Experimental chemistry has become quite expensive, particularly in the areas of development of new explosives and propellants. In addition, some chemical problems, such as characterization of transition states in chemical reactions, have no experimental techniques on which they can rely directly for answers. Our main goals of these theoretical chemical calculations are to (1) give guidance to experiments designed to develop new energetic molecules, and (2) explain experimental evidence available in terms of possible chemical reaction mechanisms.

Work has been done in the seven years of this work unit in a variety of areas. This final report is meant to be a summation of all previously published work from the work unit as well as a report on some as yet unreported calculations, those being in the explosives decomposition area. The report is broken into sections according to the chemical system being studied.

In addition to the work reported here, there has been other work in the theoretical chemistry area supporting other tasks. This other work includes a study of the potential of certain energetic plasticizer molecules in propellants<sup>1</sup> and the decomposition modes of tetrazines.<sup>2</sup>

There is much left to be done, again, particularly in the explosives decomposition area. This work unit (2303-F4-03) is being closed out because of the termination of task 2303-F4 (Molecular Dynamics). Because most of the calculations have been done on energetic materials, a new work unit (2303-F3-07), "Theoretical Calculations of Energetic Materials", is being initiated in the Energetic Materials Task (2303-F3) in FY 84. The same type of theoretical chemical calculations will be continued in that work unit.

## Chapter 2

### THEORETICAL METHODS

All of the work performed in this work unit has been with the semiempirical methods developed by Professor M. J. S. Dewar and coworkers at the University of Texas in Austin, TX. Just recently we have begun some preliminary work with the ab initio program GAUSSIAN 80, but that work will be reported in the final report of University Resident Research Program Fellow Dr. Almon G. Turner.

The first method utilized was the MINDO/3 scheme<sup>3</sup>. It is a semiempirical molecular orbital program based on an Intermediate Neglect of Differential Overlap (INDO), approximation and has the capability of optimizing geometries upon request. Dewar's more recent program, called MNDO<sup>4</sup>, is a semiempirical method based on a Neglect of Diatomic Differential Overlap (NDDO) approximation, and it, like MINDO/3 can optimize molecule geometries upon request.

Each method calculates a variety of molecular properties of interest, including equilibrium molecular geometries, heats of formation, dipole moments, atomic charges, and gradients along the potential surface. In general, MNDO results have proved superior to MINDO/3, except for certain classes of molecules, the most notable of which is nitro-containing compounds. Since this class of compounds is very important in our explosives work, we thought it wise to do calculations with both methods and compare results.

Related programs also allow searches for transition states along a reaction pathway, force constant calculations, and thermodynamic calculations. The force constant calculations are important in showing where one is on a molecular potential surface. At a stationary point, all gradients are very close to zero. If the stationary point is a stable molecule, all of

the  $3N - 6$  force constants corresponding to vibrational motion will be positive. If, however, the stationary point has one, and only one, negative force constant, it must be a transition state, with the negative force constant indicating that that mode of motion is the reaction coordinate. Two or more negative force constants indicate a "hill" on the surface, which cannot be a transition state. The results of the force constant calculations can be input into a thermodynamic program in order to get partition functions, entropies, and heat capacities.

Within each method (MNDO and MINDO/3), it is sometimes advisable to use a Unrestricted Hartree-Fock (UHF) technique if the system of interest is a reaction path or transition state in which radicals are produced from closed shell molecules. Also, UHF optimizations of transition states are often faster, and the optimized geometry of the UHF calculation is often used to begin the RHF or half-electron calculation.

Recently, Stewart and Dewar have combined all of these options into one Molecular Orbital Package (MOPAC)<sup>5</sup>. The combined package has greatly improved ease of use and is quite powerful in its capabilities.

### Chapter 3

#### ELECTROCHEMICAL CALCULATIONS

One important measurable quantity in electrochemical behavior of solutes is the half-wave potential. The quantity is a measure of how difficult it is to remove an electron (or oxidize) the species in solution. Since the calculated molecular orbital energies are directly related to the molecular ionization energy via Koopmans' theorem<sup>6</sup>, we sought to use the calculated molecular orbital energies from MNDO to predict the oxidation half-wave potentials in a room-temperature organic molten salt melt.<sup>7</sup>

We found good correlation in the study between the measured oxidation half-wave potentials and the calculated conjugation energies for a series of aromatic compounds, including some nitroaromatics in acetonitrile. The half-wave potential could be calculated from the predicted ionization energy according to:

$$E_{1/2} = 0.725 E_I - 4.95$$

$E_{1/2}$  is the measured half-wave potential in volts and  $E_I$  is the calculated ionization potential in eV.

In the room temperature molten salt, we found a similar correlation for the same set of compounds:

$$E_m = 0.725 E_I - 4.72$$

$E_m$  is the half-wave potential in the melt in volts.

The prediction for thianthrene was not as good as the other species, being off from the experimental value by about 1 volt. This discrepancy may be due to the fact that the highest occupied molecular orbital (HOMO) for thianthrene is a lone-pair orbital on the sulfur, while for all of the other molecules, the HOMO was an aromatic  $\pi$ -type orbital.

The results have been used to predict half-wave potentials for other compounds to determine their suitability as electrochemical species in the

room temperature molten salt. In some cases, the molecule is spontaneously oxidized by the melt. According to the theoretical correlation, this would happen whenever the predicted ionization potential is less than 6.51 eV, resulting in a negative half-wave potential.

The other end of the electrochemical window is also important. If the species is spontaneously reduced by the melt, it will also be unstable. The reduction potential of the molecule is related to its electron affinity, its desire to acquire an electron. In theoretical calculations, this electron affinity shows up as the energy of the lowest unoccupied molecular orbital (LUMO). We did some calculations to confirm the usefulness of MNDO to accurately predict the electron affinities of a group of molecules, and found good agreement.<sup>8</sup> These correlations have proven quite useful in establishing the electrochemical window for a variety of melt components and species on solution.

## Chapter 4

### Aluminum Calculations

The Air Force is interested in chemical properties of rocket exhaust plume species in order to determine the plume's radiation, contamination, and other effects. Many current rocket engines use fuels containing aluminum. Therefore, in order to calculate properties of various aluminum-containing molecules, it was necessary to determine MNDO parameters for aluminum and assess the accuracy of MNDO calculations for these compounds.

The parameterization work was done by Henry Rzepa at the University of Texas (Dewar's Group) and the assessment by Davis, Guidry, and Williams here at FJSRL. Both items were combined into a single journal article.<sup>9</sup> The article also included some work on boron-containing compounds.

The results indicated that the results for the aluminum-containing molecules were clearly in excess of those for compounds containing only C, H, O, and N. The average error in the heats of formation for the aluminum-containing molecules was 20.3 kcal mol<sup>-1</sup>. Several trends were noted, however. The largest errors resulted from molecules which contained oxygen as well as the aluminum (average error of 32.6 kcal mol<sup>-1</sup>). In addition, radicals were predicted to be particularly poor (average error of 31.2 kcal mol<sup>-1</sup>). As the molecule became larger, the predictions became progressively too endothermic.

Geometry predictions fared reasonably well. The only obvious trend was the underprediction of the aluminum bond lengths. The general shapes of molecules were well predicted. The errors in geometry indicate that d orbitals may be required to accurately predict the geometry of aluminum-containing molecules.

Thus the results for aluminum, while they do need some improvement, are still accurate enough to provide guidance in explaining chemical reaction mechanisms and calculating properties of aluminum-containing molecules.

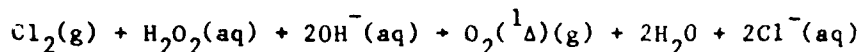


## Chapter 5

### Oxygen Singlet-Delta Calculations

One potential new chemical laser system in the near-IR involves reaction of basic hydrogen peroxide with gaseous chlorine to produce the electronically-excited  $O_2(^1\Delta)$ . The  $O_2(^1\Delta)$  can pump an atomic iodine laser<sup>10, 11</sup>. One of the major unknowns in developing these reactions into an operational chemical laser is the mechanism of the reaction in the chemical generator to produce the  $O_2(^1\Delta)$ . We have used MNDO calculations to suggest plausible mechanisms.<sup>12</sup>

The overall reaction is



The efficiency of the  $O_2$  generator is very pH-dependent, decreasing as the pH decreases. In addition, the system is complicated considerably by the two-phase nature of the process.

Specifically, our goals with MNDO were (1) to test the feasibility of proposed reaction intermediates (2) to determine whether energetically-feasible intermediates will decompose into  $O_2(^1\Delta)$  and other products and, (3) to assess the likelihood of intersystem crossing to the triplet surface to produce  $O_2(^3\Sigma)$ .

First we considered possible species present in the solution before the  $Cl_2(g)$  was added. Several acid-base equilibria are present, but both the calculations and available experimental data indicate that the predominant species in the basic hydrogen peroxide solution is the hydroperoxide ion,  $OOH^-$ . Of lesser importance is the hydroxide ion,  $OH^-$ , and some  $OCl^-$  may be present after the  $Cl_2$  is introduced to the solution.

Now we considered reactions of the  $Cl_2(g)$  with these solution species.  $Cl_2$  reacts with  $OOH^-$  without activation (according to the calculation) either to directly produce  $O_2(^1\Delta)$ ,  $HCl$ , and  $Cl^-$ , or to form a complex

$\text{HOOC}\text{Cl}_2^-$ . The direct reaction occurs only if the attack of the  $\text{Cl}_2$  is constrained to occur only on the H of the  $\text{OOH}^-$ ; otherwise the complex forms. The complex is predicted to be a stable intermediate, but there is only a fairly small barrier to dissociation of a chloride ion to form  $\text{HOOC}\text{Cl} + \text{Cl}^-$ .

In either case ( $\text{HOOC}\text{Cl}$  or  $\text{HOOC}\text{Cl}_2^-$ ), attack by any basic species in solution is predicted to break up the complex and form  $\text{O}_2(^1\Delta)$  without activation. Thus  $\text{O}_2(^1\Delta)$  can be formed without activation either by direct reaction of  $\text{Cl}_2$  with  $\text{OOH}^-$  or through the formation of an intermediate complex.

Finally, we considered the possibility of intersystem crossing to the triplet state, since this would decrease the yield of  $\text{O}_2(^1\Delta)$ . The calculations produced no feasible path for intersystem crossing in basic solution. In acidic solution, some  $\text{HOCl}$  may form, and there is a possibility of intersystem crossing in the reaction of  $\text{OOH}^-$  and  $\text{HOCl}$ .

The results showed the feasibility of using MNDO to investigate chemical reaction mechanisms in solution.

## Chapter 6

### Decomposition of Explosives and Propellants

#### Introduction

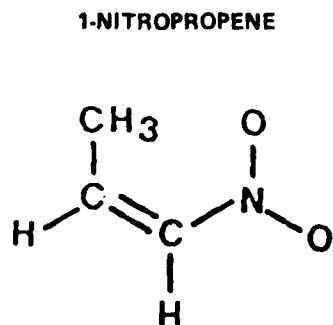
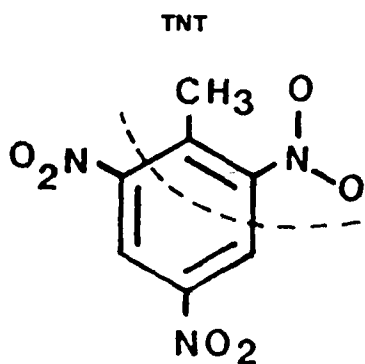
Most of the work in this area has focussed on the thermochemical decomposition of TNT, TNT-model compounds, RDX, and RDX-model compounds. However, we also studied the decomposition modes of hydrazine ( $\text{N}_2\text{H}_4$ ) in spacecraft fuel tanks at the request of AFWL. We will first report on these calculations.

#### Decomposition of $\text{N}_2\text{H}_4$

AFWL needed activation energies for all possible decomposition modes of  $\text{N}_2\text{H}_4$ . We studied breaking either the N-N bond or the N-H bond for hydrazine, the hydrazine cation, and the hydrazine dication. Results indicated that removal of a hydrogen atom had an activation energy of 77.6 kcal mol<sup>-1</sup> for hydrazine, 75.3 kcal mol<sup>-1</sup> for the cation, and 48.1 kcal mol<sup>-1</sup> for the dication. Breaking the N-N bond had an activation energy of 68.0 kcal mol<sup>-1</sup> for hydrazine, 127.2 kcal mol<sup>-1</sup> for the cation, and 108.3 kcal mol<sup>-1</sup> for the dication. These results were transmitted to AFWL and used in their modelling studies.

### TNT Decomposition

For several years the kinetics and mechanism of the thermochemical decomposition of TNT has been studied under Work Unit 2303-F3-05.<sup>13</sup> We have sought to theoretically investigate this topic as well.<sup>14</sup> Because of the size of the TNT molecule, and hence its long computation times, we have used 1-nitropropene as a model compound for TNT:



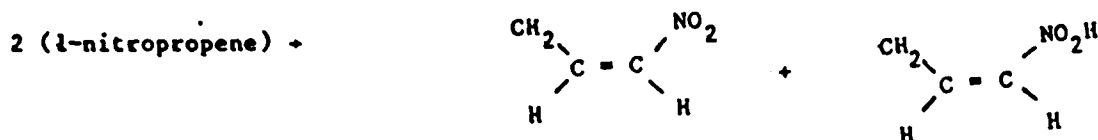
Note that the cis-1-nitropropene has the same structural features, if one is investigating reactions which involve the methyl and nitro groups, as TNT.

The TNT decomposition mechanism has been discussed for years in the literature. Based on these discussions, we chose the following six reactions as possible first steps for the TNT decomposition:

(1) Intramolecular Hydrogen Transfer



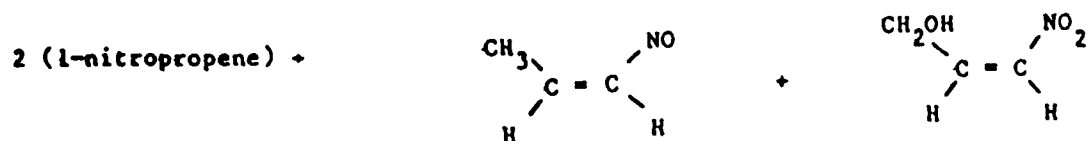
(2) Intermolecular Hydrogen Transfer



(3) Intramolecular Oxygen Insertion



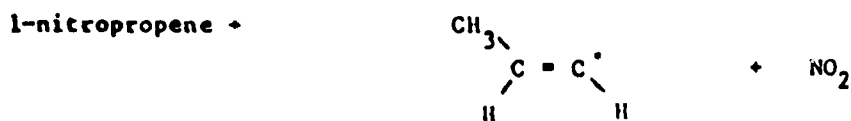
(4) Intermolecular Oxygen Insertion



(5) Nitro-Nitrite Rearrangement



(6) Nitro Group Removal



If 1-nitropropene is to be a good model for TNT, we expect the  $\Delta H^\circ$ 's for these reactions to be similar for the two systems. Since calculating heats of formation for known stationary points (reactants and products) is not overly time-consuming, we calculated  $\Delta H^\circ$ 's for all of these six reactions both with TNT and 1-nitropropene. The results are given in Table I.

TABLE I. STANDARD ENTHALPIES OF REACTION (kcal mol<sup>-1</sup>)

<u>Reaction</u>	<u>MNDO</u>			<u>MINDO/3</u>		
	<u>1-Nitropropene</u>	<u>TNT</u>	<u>Δ</u>	<u>1-Nitropropene</u>	<u>TNT</u>	<u>Δ</u>
Intra H Transfer	8.6	16.6	8.0	7.6	19.8	12.2
Inter H Transfer	16.2	16.8	0.6	38.2	38.7	0.5
Intra O Insertion	-49.5	-49.9	-0.4	-18.7	-18.4	0.3
Inter O Insertion	-51.3	-52.4	-1.1	-16.1	-21.9	-5.8
Nitro-Nitrite Rearrange- ment	-38.9	-41.1	-2.2	-11.8	-7.5	4.3
Nitro Group Removal	29.8	26.9	-2.9	41.4	62.1	20.7

We note that in general there is good agreement between the 1-nitropropene result and the TNT result for either method. There is a large discrepancy, however, between the MNDO and MINDO/3 results for most reactions. When they differ, we would expect the MINDO/3 results to be better, since MNDO gives poor results for heats of formation for nitro-containing compounds.<sup>15</sup> The only really bad result that MINDO/3 gives is for NO<sub>2</sub>, making it about 25 kcal mol<sup>-1</sup> too stable. Thus the  $\Delta H^\circ$  for the nitro group removal will be underestimated. Since MNDO generally predicts nitro compounds too unstable, it will in general make the predicted  $\Delta H^\circ$  too exothermic for any reaction which involves changing the nitro group in some way. This is borne out by comparing the MNDO and MINDO/3 results.

Since 1-nitropropene does indeed correlate well with TNT in terms of  $\Delta H^\circ$ 's, it should also serve as a good model for the activation enthalpies of these processes. Transition states were located by defining a reaction coordinate for each reaction, finding the point of maximum enthalpy, and then using a transition state location program which minimizes the sum of squares of the gradients. Each transition state was identified as a transition state by running a force constant calculation which produced one, and only one, negative force constant. Table II gives the calculated activation enthalpies for each reaction.



TABLE II. ACTIVATION ENTHALPIES (kcal mol<sup>-1</sup>) FOR 1-NITROPROPENE SYSTEM

<u>Reaction</u>	<u>MNDO</u>	<u>MINDO/3</u>
Intra H Transfer	63.7 (59.5)	43.4 (43.4)
Inter H Transfer	-- (50.4)	-- (39.6)
Intra O Insertion	127.7	49.9
Inter O Insertion	108.7	44.4
Nitro-Nitrite Rearrange- ment	51.6	35.0
Nitro Group* Removal	29.8	41.4

( ) = UHF Calculation

\* No true transition state;  $\Delta H^\circ$  assumed to be the reaction  $\Delta H^\circ$ .

The transition state obtained for the intramolecular hydrogen atom transfer of a hydrogen atom from the  $\text{CH}_3$  end of the three carbon chain to the nitro group is a cyclic structure wherein the hydrogen atom-carbon atom bond has been elongated from 1.10Å to 1.34Å (bond order of 0.42). The initial stages of O-H bond formation can be identified with the hydrogen oxygen distance of 1.17Å (bond order of 0.44). The transition state is non-planar with the hydrogen being transferred about 0.5Å out of the plane formed by the three carbon atoms. The force constant calculation gave excellent results: one large negative eigenvalue for the reaction coordinate and six close-to-zero results for the translations and rotations (all less than  $6 \text{ cm}^{-1}$ ). The reaction coordinate corresponded primarily to motion of the hydrogen being transferred.

The calculated activation enthalpy was somewhat higher for MNDO than MINDO/3 ( $63.7 \text{ kcal mol}^{-1}$  compared to  $43.4 \text{ kcal mol}^{-1}$ ). This is consistent with MNDO normally giving slightly high activation enthalpies for hydrogen transfer reactions. The MINDO/3 result is consistent with the experimental activation energy and thus this process cannot be ruled out as a first step in the thermochemical decomposition on the basis of this calculated activation energy. We would expect the TNT activation enthalpy to be several  $\text{kcal mol}^{-1}$  higher; however, because of the loss of the aromatic character of the ring as TNT converts to the product state. This effect, of course, will not show up in our 1-nitropropene model compound. Because of the possible diradical character of the product, we also optimized the transition state using an UHF type calculation. For MINDO/3, no spin imbalance was calculated and the results were the same as the RHF results. MNDO gave a slightly lower value for the activation enthalpy with UHF, but the difference was not significant.

The transition state for the intermolecular hydrogen transfer was calculated using UHF. The product of this reaction is two radicals and

attempts to optimize an RHF transition state resulted, as could be expected, in the separated reactants. In contrast to the intramolecular hydrogen transfer transition state, which was almost symmetrical in terms of the C-H and O-H bond orders, this intermolecular transition state shows that the C-H bond is more than half-broken (C-H distance is 1.36Å, with a bond order of 0.30) while the O-H bond is more appreciably formed (O-H distance is 1.07Å, with a bond order of 0.53). The C-H-O bond angle is 166°, approaching linearity. The force constant calculation gave one large negative eigenvalue for the reaction coordinate, but the translations and vibrations did mix appreciably with the low-lying vibrations (frequencies for the translations and rotations exceeded 100 cm<sup>-1</sup>). This mixing is not surprising considering the loosely bound nature of this bimolecular transition state, and it should not qualitatively affect the conclusions. Once again, the reaction coordinate indicated the motion to consist primarily of hydrogen atom translations.

Again, the calculated activation enthalpy for MNDO is somewhat higher than for MINDO/3 (50.4 kcal mol<sup>-1</sup> vs. 39.6 kcal mol<sup>-1</sup>), following the trend that MNDO overpredicts activation enthalpies for hydrogen transfer reactions. The MINDO/3 result for this reaction is also consistent with the experimental activation energy, although MINDO/3 UHF results typically may underestimate the activation enthalpy by several kcal mol<sup>-1</sup>. Even so, the agreement with the experimental number is quite good.

In the MINDO/3 transition state for the intramolecular oxygen insertion from the nitro group into a C-H bond of the methyl group, the N-O bond is stretched (distance of 1.35Å, bond order of 0.86), the C-H bond is stretched (distance of 1.25Å, bond order of 0.59), thus C-O bond is partially formed (distance of 1.63Å, bond order of 0.29), and the O-H bond is partially formed (distance of 1.22Å, bond order of 0.29). The geometry of the transition state is slightly non-planar, with the inserted oxygen atom and the

hydrogen atom both about 0.1Å out of the plane formed by the three carbon atoms. Indeed, the first attempt to optimize this transition state with MINDO/3 produced a planar geometry, but the presence of more than one negative force constant indicated that the structure was not a true transition state. The force constant calculation on the true transition state had only one negative force constant, with each of the translational and rotational modes having frequencies less than  $10\text{ cm}^{-1}$ . The reaction coordinate corresponded to motion of all of the atoms involved in either bond-making or bond-breaking, with the oxygen and the hydrogen showing the largest effects. Interestingly, there was virtually no difference in the calculated heats of formation between the planar and non-planar structure. The MNDO result was not quite as good. In spite of repeated attempts to displace the stationary point calculated by MNDO from planarity, we were not successful. The result is a planar stationary point which we believe to be very near the true transition state, but which nevertheless has two negative eigenvalues in the force constant matrix: one (corresponding to the true reaction coordinate) of  $1733\text{ cm}^{-1}$  and the other (corresponding primarily to torsional motion of the hydrogen in and out of the plane of the molecule) of  $303\text{ cm}^{-1}$ .

There is a large difference between the calculated enthalpies of activation for MNDO and MINDO/3 ( $127.7\text{ kcal mol}^{-1}$  vs.  $49.9\text{ kcal mol}^{-1}$ ), even though the overall geometries are similar. Based on previously-discussed rationale, the MINDO/3 results are more believable. The MINDO/3 enthalpy of activation is slightly larger than the experimented activation energy, but the  $10\text{ kcal mol}^{-1}$  difference does not completely rule this step out as a possible first step. We think, however, that it is less likely than the hydrogen transfer steps previously discussed.

Compared with the intramolecular insertion transition state, in the case of the intermolecular oxygen insertion, the reaction has proceeded more toward

product; the N-O bond is stretched (distance of 1.38Å, bond order of 0.75), the C-H bond is stretched (distance of 1.29Å, bond order of 0.48), the C-O bond is partially formed (distance of 1.66Å, bond order of 0.35), and the O-H bond is partially formed (distance of 1.11Å, bond order of 0.39). The N-O-C bond angle is 158°, approaching linearity. The force constant calculation gives a single negative force constant, with rather poor separation of the translational and rotational modes (maximum frequency of 69  $\text{cm}^{-1}$ ). Again, this mixing with low-lying vibrations is not uncommon for bimolecular transition states. The reaction coordinate consists of motion primarily by the atoms involved in bond-breaking and bond-making, but there are minor contributions from many of the other modes.

Like the intramolecular oxygen insertion, there is a large discrepancy between MNDO and MINDO/3 in the calculated enthalpies of activation for this intermolecular oxygen insertion (108.7  $\text{kcal mol}^{-1}$  vs. 44.4  $\text{kcal mol}^{-1}$ ). Again, assuming the MINDO/3 value to be more accurate, this calculated activation enthalpy is consistent with the experimental activation energy. This process is quite likely to be taking place in the initial stages of TNT decomposition.

In the nitro-nitrite rearrangement, one of the oxygens inserts into the C-N bond, resulting in the structure C-O-N-O. The transition state shows stretching of the C-N bond (distance of 1.45Å, bond order of 0.71), stretching of the N-O partial double bond in the nitro group toward the single bond in the product (distance of 1.30Å, bond order of 1.19), and partial formation of the C-O bond (distance of 1.53Å, bond order of 0.45). The force constant calculation gives a single negative eigenvalue of frequency 705  $\text{cm}^{-1}$ , with good separation of the translational and rotational modes (maximum frequency of 9  $\text{cm}^{-1}$ ). The reaction coordinate consists of movement primarily by the three atoms involved, C, N, and O.

The results for the activation enthalpies are  $35.0 \text{ kcal mol}^{-1}$  and  $51.6 \text{ kcal mol}^{-1}$  for MINDO/3 and MNDO, respectively. Both values are not far removed from the experimental activation energy, making this process a feasible first step on an activation enthalpy basis.

The last process considered was a simple C-N bond fission, resulting in the  $\text{C}_3\text{H}_5$  radical and  $\text{NO}_2$ . A reaction path calculation failed to produce a transition state, meaning that the reverse reaction should process without activation, a common occurrence for a radical recombination reaction. Thus, the activation enthalpy and the reaction enthalpy are one and the same. The results are  $29.8 \text{ kcal mol}^{-1}$  for MNDO and  $41.4 \text{ kcal mol}^{-1}$  for MINDO/3. Both values make the C-N bond scission look feasible when compared with the experimental activation energy, but we feel that both numbers are in error. MNDO results for heats of formation of nitroaromatics generally are far too endothermic,<sup>15</sup> destabilizing the reactant and making the activation enthalpy too small. On the other hand, MINDO/3 gravely overstabilizes  $\text{NO}_2$  by about  $25 \text{ kcal mol}^{-1}$ , again making the activation enthalpy too small. If one corrects the MINDO/3 result for this known error for  $\text{NO}_2$ , an activation enthalpy of about  $65 \text{ kcal mol}^{-1}$  is obtained. This number agrees with the  $70 \text{ kcal mol}^{-1}$  value one obtains for the C-N bond strength in nitrobenzene if the experimental heats of formation for nitrobenzene and  $\text{NO}_2$ , and the MNDO-calculated value for phenyl radical are used. This  $70 \text{ kcal mol}^{-1}$  value is also in the area of a C-N bond strength according to conventional organic chemistry wisdom. Thus, we feel that a simple C-N bond fission is not possible as a first step in the thermochemical decomposition of TNT.

Cis-1-nitropropene is a good theoretical model for studying TNT thermochemical decomposition. It reproduces all of the major structural features of a nitro group being ortho to the methyl group in TNT. Of all of the possible reaction steps we considered, only the intramolecular hydrogen

transfer changes the aromaticity of the TNT system, making our 1-nitropropene model not quite as good for that case. Even so, we are able to deduce qualitative trends of this effect.

MINDO/3 results do appear to be more reliable than the MNDO results. We cannot explain the abnormally high values of the activation enthalpies that MNDO gives for the oxygen transfer steps. It is quite feasible that, in spite of repeated attempts, we have still not obtained the transition states for these processes with MNDO. In the other cases, the MINDO/3 and MNDO results are similar.

Our original goal was to draw conclusions about possible first steps of TNT thermochemical decomposition by comparing our theoretical results with the EPR and IDSC results. On an activation energy basis, several processes appear to be likely: both hydrogen transfers, both oxygen transfers, and the nitro-nitrite rearrangement. The fairly large isotope effect, however, is difficult to explain with anything but the two hydrogen transfer steps, although we are currently calculating deuterium isotope effects for all of these steps. The EPR signals indicate that radicals must be involved, and the spectrum shows two nitrogens and five hydrogens. The intermolecular hydrogen transfer has the attraction that it produces radicals directly, but not with the required two nitrogens. HONO loss from the hydrogen transfer product does result in a radical with the required two nitrogens and five hydrogens, and further work is in progress to determine the feasibility of these follow-on steps. On the other hand, intramolecular hydrogen transfer followed by HONO loss would result in a radical, but with two nitrogens and only four hydrogens.

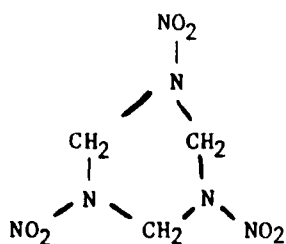
The intermolecular hydrogen transfer process is consistent with all of the known experimental facts for TNT thermochemical decomposition. Thus, we feel that it is a major process early in the decomposition. The low activation enthalpies calculated for several other steps, however, make it probable that

these other processes go on just as well. Indeed, all of previous studies on TNT thermochemical decomposition indicate that the system is quite complicated, particularly in light of the multitude of intermediate products. Our calculations certainly indicate the complexity of the system.

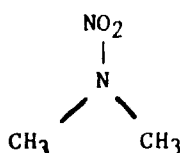


## Decomposition of RDX

The chemistry of the heterocyclic nitramine 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) is of great interest because of its use as an explosive.



RDX



DMNA

The purpose of this work was to perform computer modeling of possible thermal decomposition paths of dimethylnitramine (DMNA). The reason that DMNA was chosen was because of its similarity to RDX while being much simpler to model with the computer. The following list explains all the decomposition paths which have been worked on and which have been considered of interest to this date.

1. Breaking the N-N bond and dissociating nitrogen dioxide.
2. Breaking the N-N bond of the anion and dissociating  $\text{NO}_2^-$ .
3. Breaking a C-N bond and dissociating a  $\text{CH}_3$  group.
4. Breaking a N-O and dissociating an oxygen atom.
5. Breaking a C-H bond and dissociating a hydrogen atom.
6. The addition of a hydrogen atom to the  $\text{NO}_2$  group.
7. The intermolecular transfer of a hydrogen atom between 2 DMNA molecules creating an O-H bond and breaking a C-H bond.
8. Breaking the N-N bond and releasing the HONO group created in 6 or 7 above.

9. The intramolecule of a hydrogen from a methyl group to the nitro group breaking a C-H bond and creating an OH bond.
10. Breaking the N-N bond and releasing the HONO group created in 9 above.
11. Rearranging the nitro group to a nitrite.
12. Intramolecular insertion of an oxygen atom from the nitro group to a methyl group.
13. The insertion of an oxygen atom into the methyl group.
14. The intermolecular insertion of an oxygen atom and from the nitro group of one DMNA molecule into the methyl group of a second DMNA molecule.

Table III shows a summary of the calculations run to date using the MNDO and MINDO/3 methods. Of note is the significant discrepancies between the two methods in a number of cases. These discrepancies have not been resolved at this time. This work will be continued under the new work unit.

TABLE III. Results of DMNA Calculations

Path	<u>MNDO</u>		<u>MINDO/3</u>	
	<u><math>\Delta H</math></u>	<u>Activation Energy</u>	<u><math>\Delta H</math></u>	<u>Activation Energy</u>
1. Break NO <sub>2</sub>	2.0	22.5	23.1	*
2. Break NO <sub>2</sub> (-)	-21.3	1.6	48.7	*
3. Break CH <sub>3</sub>	57.2	58.7 <sup>2</sup>	44.8	*
4. Break O	33.7	94.7	70.6	*
5. Break H	87.1	79.1 <sup>2</sup>	87.9	*
6. H Addition	-63.6	7.4	-55.3	*
7. H Transfer				
Intermolecular	21.4	~76	56.9	*
8. HONO Break	-20.9	6.5	25.0	*
9. H Transfer				
Intramolecular	13.0	~66	24.7	*
10. HONO Break	58.9 <sup>1</sup>	*	14.8 <sup>1</sup>	*
11. NO <sub>2</sub> Rearrange	-22.4	68.8	37.4	*
12. O Transfer	-69.9	125.4	-40.8	*
Intramolecular				
13. O Addition	*	*	*	*
14. O Transfer	*	*	*	*
Intermolecular				

\* Not Finished

1. Product is not stable and optimized geometry only approximate.
2. There is probably no transition state with these reactions.

## Chapter 7

### Sulfur Nitrogen Calculations

#### Introduction

At the present time approximately fifty molecules and ions (both positive and negative) composed solely of sulfur and nitrogen atoms are known. They range in composition from simple diatomic and triatomic species such as  $\text{NS}^+$  and  $\text{NNS}$  to cyclic species such as  $\text{S}_4\text{N}_4^{2+}$ ,  $\text{S}_3\text{N}_3^-$ ,  $\text{S}_2\text{N}_2$  and extend on to polyhedral moieties such as  $\text{S}_4\text{N}_4$ ,  $\text{S}_4\text{N}_5^-$ ,  $\text{S}_6\text{N}_4$ , etc. Ultimately they are all synthesized from the parent material, tetrasulfur tetranitride which in turn is readily available from the common commercial chemicals, sulfur dichloride and ammonia. Species are known in all three states of matter, gaseous, liquid, and solid (including polymers). Potential applications exist in the areas of liquid and solid, slow and rapidly burning propellants, explosives, detonators, electrochemical battery applications, polymeric materials (electrical conducting and as insulators) and in materials. Applications to each of these areas are outlined below.

#### Thermodynamic Considerations

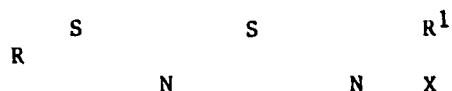
The literature has long documented the explosive (endothermic) nature of the following materials:  $\text{S}_4\text{N}_4$ , tetrasulfur tetranitride (solid) (thermal and mechanical instability in the solid state);  $\text{S}_2\text{N}_2$ , disulfur dinitride (solid) (thermal instability);  $\text{S}_4\text{N}_2$ , 1-3 tetrasulfur dinitride, (liquid)  $\text{S}_3\text{N}_3^-$ , trisulfur trinitride, and several other materials. A recent study at the U. S. Air Force, F. J. Seiler Research Laboratory indicated that every sulfur-nitrogen compound known possesses a large positive  $\Delta H_f^\circ$  relative to molecular nitrogen and sulfur at 25°C. Since  $\Delta S^\circ$  for most decomposition reactions can be expected to be positive, reactions which lead to a fragmentation of the parent molecule, and the production of either  $\text{N}_2$ ,

$S_8$ , or oxidized forms thereof are expected to be strongly exothermic. The observed explosive nature of these materials supports this conclusion. The above listed materials offer a wide range of potential solid state or liquid state explosives or propellants. The mechanical sensitivity of  $S_4N_4$  suggests application as a potential detonating agent. There have been no scientific studies to date which attempt to evaluate these materials with respect to the specific impulse available; interaction with specific oxidizers, burn rate, etc.

#### Electrochemical Considerations

A large variety of positive and negative ions and thus salts of sulfur nitrogen compounds are known. They range in structure from planar systems such as  $S_4N_4^{2+}$ ,  $S_4N_3^+$ ,  $S_5N_5^+$  and  $S_3N_3$  to polyhedral ions such as  $S_4N_5^-$ ,  $S_4N^-$ ,  $S_6N_4^{2+}$ . They are generally prepared in non aqueous solvents such as  $CH_3CN$ , DMF,  $SbF_5$  and others. Nothing is known of their behavior in molten salt systems. There have been a few polarographic studies carried out. The wide range of species available suggest that they might offer potential application as supporting electrolytes. Many of the species possess ionization potentials in excess of 10 eV and relatively low electron affinities. In the absence of experimental data it is difficult to be more specific, but the diverse range of species and structures available suggest that this might be a fruitful area of research.

Extensive studies of the electrical properties of polymeric sulfur nitride,  $(SN)_x$  have been carried out and will not be discussed here. However, it should be pointed out that synthetic methods are available for the preparation of substituted materials of the general type



$\text{R}', \text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$

$\text{X} = 1, 2, 3, 4 \dots$

which can be expected to show interesting properties such as metallic like character, semiconductivity, high melting points, etc.

#### Application to the Materials Area

The ability synthetically to produce addition and substitution products of most of the sulfur nitrides gives access to a wide area of materials of possible diverse application. The area is spanned by polymeric materials such as  $(\text{HOSN})_x$  and its derivatives, halogen substituted compounds such as  $\text{NSF}$ ,  $\text{S}_4\text{N}_4\text{F}_4$ ,  $\text{S}_3\text{N}_2\text{Cl}_2$ ,  $\text{S}_4\text{N}_3\text{Cl}$  and others, as well as interesting non classical materials such as  $\text{Hg}_5(\text{SN})_8$ , etc. Applications to the areas of toxic materials, herbicides, fungicides, slimicides, oxidation inhibitors, surfactants, etc almost certainly exist.

The calculations done in this work unit were in support of those possible applications.

The mechanism of polymerization of  $\text{S}_2\text{N}_2$  was studied via MNDO type molecular orbital calculations.<sup>16</sup> It was postulated that the reaction proceeds via a cleavage of the  $\text{S}_2\text{N}_2$  ring with the formation of a change type intermediate in within a triplet or singlet state. Structures of and activation energies were found for the two intermediates and the triplet state path was found to be energetically preferable.

The isomerization reaction  $\text{HNSO} \rightarrow \text{HOSN}$  was studied by MNDO molecular orbital calculations.<sup>17</sup> The S-thiazyl hydroxide form was found to be lower in energy by 7 kcal mol<sup>-1</sup>. The transition state was characterized with an activation energy of 75 kcal mol<sup>-1</sup>. The electronic structure of the reactant, product and transition state were analyzed using LMO's.

The electronic structure of the  $\text{S}_3\text{N}_3^-$  anion was studied using localized molecular orbitals derived from CNDO/2 canonical M.O.'s.<sup>18</sup> Particular attention is given to the nature of the sigma-pi separation of electronic charge. The calculation suggested that the anion is best described as a  $4\pi$  electron system in contrast to the  $10\pi$  model previously suggested. The electronic structure of the recently discovered  $\text{S}_4\text{N}_4^{2-}$  ion was studied by MNDO and LMO methods.<sup>19</sup> The planar ion was demonstrated to conform to a  $10\pi$  Huckel-type moiety. The sulfur trinitride bis(triphenylphosphite) nickel (II) dihydrate compound was synthesized and characterized by spectral methods.<sup>20</sup> It was shown to be the first example of material containing the  $\text{SN}_3^-$  ligand.

The general area of the electronic structure of binary sulfur-nitrogen molecules and ions was studied using density functional theory and MNDO types of approximate wave functions. A detailed discussion of the identification of equivalent charge sites within a molecule was presented. This work was presented as part of "Symposium on Application of Topology and Graph Theory to Chemistry", University of Georgia, April 1983 and has been published in book form as part of the symposium volume.

All known binary compounds of sulfur-nitrogen were examined by MNDO types of molecular orbital calculations<sup>21</sup>. The standard enthalpy of formation was calculated relative to that of  $\text{S}_4\text{N}_4$ . The materials were shown to be highly endothermic. Possible application to AFOSR needs are discussed.

## REFERENCES

- 1) L. P. Davis, R. A. Hildreth, and M. L. Druelinger, Predicted Performance of Energetic Plastizer Formulations, FJSRL-TR-80-0015, June 1980.
- 2) M. L. Druelinger, L. P. Davis, P. E. Vorndam, D. E. Easler, and L. A. Connell, "Synthesis and Decomposition of Nitrated Tetrazines", presentation given at the 184th National American Chemical Society meeting in Kansas City, MO, 15 Sep 1982.
- 3) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, J. Am. Chem. Soc., 1975, 97, 1285.
- 4) M. J. S. Dewar and W. J. Thiel, J. Am. Chem. Soc., 1977, 99, 4899.
- 5) Quantum Chemistry Program Exchange Bulletin, Department of Chemistry Indiana University, Volume 3, Number 2, May 1983.
- 6) T. Koopmans, Physica, 1933, 1, 104.
- 7) L. P. Davis, C. L. Hussey, L. A. King, and J. S. Wilkes, Prediction of Oxidation Half-Wave Potentials by MNDO Calculations, FJSRL-TR-80-0011, May 1980.
- 8) L. P. Davis and R. E. Nelson, "MNDO Values of Electron Affinities and ESR Coupling Constants", presentation given at the ACS Meeting-in-Miniature, Denver, CO, 3 May 1980.
- 9) L. P. Davis, R. M. Guidry, J. R. Williams, M. J. S. Dewar, and H. S. Rzepa, J. Comput. Chem., 1981, 2, 433.
- 10) W. E. McDermott, N. R. Pchelkin, D. J. Benard, and R. R. Bousek, Appl. Phys. Lett., 1978, 32, 469.
- 11) D. J. Benard, W. E. McDermott, N. R. Pchelkin, and R. R. Bousek, Appl. Phys. Lett., 1979, 34, 40.
- 12) D. M. Storch, C. J. Dymek, Jr., and L. P. Davis, J. Am. Chem. Soc., 1983, 105, 1765.
- 13) R. M. Guidry and L. P. Davis, Thermochimica Acta, 1979, 32, 1.
- 14) A. G. Turner and L. P. Davis, "Thermal Decomposition of TNT: Use of 1-Nitropropene to Model the Initial Stages of Decomposition", in preparation for publication.
- 15) R. M. Guidry and L. P. Davis, MINDO/3 and MNDO Calculations for Nitro-Compounds, FJSRL Technical Report, in preparation for publication.
- 16) A. G. Turner, in preparation for publication.
- 17) J. J. Oleksik and A. G. Turner, Inorg. Chimica Acta, 1982, 59, 165.



(18) A. A. Bhattacharyya, A. Bhattacharyya and A. G. Turner, Inorg. Chim. Acta, 1982, 64, L33.

(20) A. A. Bhattacharyya and A. G. Turner, Inorg. Chem. Acta, 1983, 76, L97.

(21) S. Sensarma and A. G. Turner, Inorg. Chem. Acta, 1982, 64, L161.

